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SUPPORTING INFORMATION

Rhodium/Phosphoramidite-Catalyzed Asymmetric Arylation of Aldehydes with Arylboronic Acids

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General remarks: All air and moisture sensitive manipulations were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. ^1H -NMR, ^{31}P -NMR, and ^{13}C -NMR spectra were recorded on a Varian 400 (400, 162, and 101 MHz) in CDCl_3 . Mass spectra (HRMS) were recorded on an AEI MS-902. Optical rotations were measured on a Schmidt and Haensch Polartronic MH8. $\text{Rh}(\text{acac})(\text{C}_2\text{H}_4)_2$ was purchased from Strem and used without further purification. Dioxane was distilled from sodium. All other chemicals were purchased from Acros and used as received unless stated otherwise. Flash chromatography was performed using silica gel 60 Å (Merck, 230-400 mesh). Phosphoramidite ligands **L1**¹ and **L2**² were prepared according to literature procedures.

Catalytic arylboronic acid addition reactions

General procedure for Table 1, entries 1-7. In a flame dried Schlenk tube flushed with nitrogen, 1.55 mg (6.0 μmol , 3 mol%) of $\text{Rh}(\text{acac})(\text{C}_2\text{H}_4)_2$ and 14.0 μmol (7.5 mol%) of one of the enantiomers of phosphoramidite **L1** were dissolved in 2 mL of solvent. After stirring for 15 min at room temperature, 0.2 mmol of substrate **1a** and 0.6 mmol of phenylboronic acid (**2a**, 3 equiv) were added and the resulting mixture was stirred at reflux. After 4 h the reaction mixture was cooled to RT and quenched with 2 mL of a 12.5% aqueous ammonia solution. After 20 minutes the water-layer was extracted with 3 x 5 mL of ethylacetate, the combined organic layers dried on Na_2SO_4 , and evaporated under reduced pressure.

General procedure for Table 2, entries 1-11. In a flame dried Schlenk tube flushed with nitrogen, 1.55 mg (6.0 μmol , 3 mol%) of $\text{Rh}(\text{acac})(\text{C}_2\text{H}_4)_2$ and 6.5 μmol (3.5 mol%) phosphoramidite (*S,S*)-**L2** were dissolved in 2 mL of 2-propanol. After stirring for 15 min at room temperature, 0.2 mmol of substrate **1** and 0.6 mmol of arylboronic acid **2** (3 equiv) were added and the resulting mixture was stirred at reflux. After 4 h the reaction mixture was cooled to RT and evaporated under reduced pressure. Products were purified by flash chromatography (SiO_2 , pentane:EtOAc = 20:1).

(R)-(4-chlorophenyl)phenylmethanol (3a). Obtained as a solid in 91% isolated yield (Table 2, entry 1); mp 47.4-48.4 °C; ^1H NMR (CDCl_3) δ = 7.21-7.30 (m, 9H), 5.75 (s, 1H), 2.11 (bs, 1H); ^{13}C NMR

(CDCl₃) δ = 143.40, 142.17, 133.25, 128.62 (2), 128.57 (2), 127.84 (3), 126.49 (2), 75.59; HRMS calcd for C₁₃H₁₁O³⁷Cl: m/z 220.0469, found: 220.0461; The ee was determined on a Chiralcel AD column with heptane : isopropanol = 95 : 5, flow = 1.0 mL/ min. Retention times: 11.3 [(R)-enantiomer] and 12.1 [(S)-enantiomer] min; $[\alpha]^{20}_D$ = -10.4 (c 1.08, CHCl₃, Table 2, entry 1, 60%), lit.³ $[\alpha]^{26}_D$ = -18.6 (c 0.86, CHCl₃, 94%, (R)).

(R)-(4-trifluoromethylphenyl)phenylmethanol (3b). Obtained as a solid in 94% isolated yield (Table 2, entry 2); mp 71.9-73.0 °C; ¹H NMR (CDCl₃) δ = 7.45-7.56 (m, 4H), 7.21-7.31 (m, 5H), 5.83 (s, 1H), 2.19 (bs, 1H); ¹³C NMR (CDCl₃) δ = 147.48, 143.13, 129.21 (q, J_{CF} = 32.1 Hz), 128.75 (2), 128.08, 126.64 (2), 126.61 (2), 125.39 (2q, J_{CF} = 3.7 Hz), 124.19 (q, J_{CF} = 286.4 Hz), 75.75; HRMS calcd for C₁₄H₁₁OF₃: m/z 252.0762, found: 252.0774; The ee was determined on a Chiralcel AD column with heptane : isopropanol = 98 : 2, flow = 1.0 mL/ min. Retention times: 17.0 [(R)-enantiomer] and 20.2 ((S)-enantiomer) min; $[\alpha]^{20}_D$ = -19.4 (c 1.05, CHCl₃, Table 2, entry 2, 51% ee), lit.⁴ $[\alpha]^{22}_D$ = -34.6 (c 0.19, C₆H₆, 94%, (R)).

(R)-(4-phenylphenyl)phenylmethanol (3c). Obtained as a solid in 93% isolated yield (Table 2, entry 3); mp 74.0-74.6 °C; ¹H NMR (CDCl₃) δ = 7.21-7.57 (m, 14H), 5.84 (s, 1H), 2.38 (bs, 1H); ¹³C NMR (CDCl₃) δ = 143.69, 142.77, 140.71, 140.41, 128.71 (2), 128.50 (2), 127.57, 127.23, 127.18 (2), 127.02 (2), 126.93 (2), 126.51 (2), 75.96; HRMS calcd for C₁₉H₁₆O: m/z 260.1201, found: 260.1203; The ee was determined on a Chiralcel AD column with heptane : isopropanol = 98 : 2, flow = 1.0 mL/ min. Retention times: 36.8 [(S)-enantiomer] and 41.9 min [(R)-enantiomer]; $[\alpha]^{20}_D$ = -3.2 (c 1.01, CHCl₃, Table 2, entry 3, 59% ee).

(R)- and (S)-(4-tolyl)phenylmethanol (3d). The (R)-enantiomer was obtained as a solid in 80% isolated yield (Table 2, entry 4) and the (S)-enantiomer was obtained as a solid in 93% isolated yield (Table 2, entry 6); mp 51.4-52.9 °C; ¹H NMR (CDCl₃) δ = 7.09-7.33 (m, 9H), 5.76 (s, 1H), 2.29 (s, 3H), 2.19 (bs, 1H); ¹³C NMR (CDCl₃) δ = 143.89, 140.90, 137.22, 129.13 (2), 128.39 (2), 127.40, 126.47 (2), 126.40 (2), 76.03, 21.07; HRMS calcd for C₁₄H₁₄O: m/z 198.1045, found: 198.1053; The ee was determined on a Chiralcel AD column with heptane : isopropanol = 98 : 2, flow = 1.0 mL/ min. Retention

times: 20.6 [(R)-enantiomer] and 21.7 [(S)-enantiomer] min; $[\alpha]^{20}_D = +5.2$ (c 0.92, CHCl₃, Table 2, entry 4, 60% ee), $[\alpha]^{20}_D = -4.0$ (c 0.76, CHCl₃, Table 2, entry 6, 47% ee), lit.⁵ $[\alpha]^{20}_D = +8.4$ (c 0.50, CHCl₃, 97% ee, (R)).

(R)-(4-methoxyphenyl)phenylmethanol (3e). Obtained as a viscous oil in 61% isolated yield (Table 2, entry 5); ¹H NMR (CDCl₃) δ = 7.20–7.34 (m, 7H), 6.82 (m, 2H), 5.76 (s, 1H), 3.74 (s, 3H), 2.20 (bs, 1H); ¹³C NMR (CDCl₃) δ = 158.99, 143.96, 136.12, 128.40 (2), 127.86 (2), 127.38, 126.35 (2), 113.82 (2), 75.76, 55.24; HRMS calcd for C₁₄H₁₄O₂: m/z 214.0994, found: 214.0992; The ee was determined on a Chiralcel AD column with heptane : isopropanol = 95 : 5, flow = 1.0 mL/ min. Retention times: 16.7 [(R)-enantiomer] and 17.8 [(S)-enantiomer] min; $[\alpha]^{20}_D = +16.9$ (c 0.44, C₆H₆, Table 2, entry 5, 60% ee), lit.⁶ $[\alpha]^{20}_D = +18.7$ (c 1.86, C₆H₆, (R)).

(R)-(3-methoxyphenyl)phenylmethanol (3f). Obtained as an oil in 96% isolated yield (Table 2, entry 8); ¹H NMR (CDCl₃) δ = 7.19–7.35 (m, 6H), 6.90 (m, 2H), 6.77 (m, 1H), 5.74 (s, 1H), 3.74 (s, 3H), 2.38 (bs, 1H); ¹³C NMR (CDCl₃) δ = 159.64, 145.41, 143.61, 129.44, 128.42, 128.19, 127.52, 126.46 (2), 118.84, 112.89, 112.02, 76.06, 55.14; HRMS calcd for C₁₄H₁₄O₂: m/z 214.0994, found: 214.1002; The ee was determined on a Chiralcel AD column with heptane : isopropanol = 98 : 2, flow = 1.0 mL/ min. Retention times: 34.3 [(S)-enantiomer] and 36.0 [(R)-enantiomer] min; $[\alpha]^{20}_D = -8.7$ (c 0.99, CHCl₃, Table 2, entry 8, 61% ee).

(R)-(2-methoxyphenyl)phenylmethanol (3g). Obtained as an oil in 89% isolated yield (Table 2, entry 9); ¹H NMR (CDCl₃) δ = 7.18–7.36 (m, 7H), 6.83–6.93 (m, 2H), 6.02 (s, 1H), 3.76 (s, 3H), 2.99 (bs, 1H); ¹³C NMR (CDCl₃) δ = 156.70, 143.24, 131.94, 128.67, 128.11 (2), 127.82, 127.10, 126.51 (2), 120.76, 110.73, 72.21, 55.36; HRMS calcd for C₁₄H₁₄O₂: m/z 214.0994, found: 214.1003; The ee was determined on a Chiralcel AD column with heptane : isopropanol = 95 : 5, flow = 1.0 mL/ min. Retention times: 13.1 (minor) and 14.2 (major) min; $[\alpha]^{20}_D = +18.2$ (c 0.77, CHCl₃, Table 2, entry 9, 50% ee).

(R)-(1-naphthyl)phenylmethanol (3h). Obtained as a viscous oil in 67% isolated yield (Table 2, entry 10); ¹H NMR (CDCl₃) δ = 7.99 (m,

1H), 7.74-7.85 (m, 2H), 7.59 (m, 1H), 7.21-7.47 (m, 8H), 6.49 (s, 1H), 2.16 (bs, 1H); ^{13}C NMR (CDCl_3) δ = 143.05, 138.73, 133.88, 130.63, 128.73, 128.50, 128.45, 128.29, 127.64, 127.00, 126.11, 125.94, 125.56, 125.29, 124.57, 123.94, 73.63; HRMS calcd for $\text{C}_{17}\text{H}_{14}\text{O}$: m/z 234.1045, found: 234.1053; The ee was determined on a Chiralcel AD column with heptane : isopropanol = 98 : 2, flow = 1.0 mL/ min. Retention times: 35.1 [(S)-enantiomer] and 38.8 [(R)-enantiomer] min; $[\alpha]^{20}_{\text{D}}$ = +29.6 (c 0.54, C_6H_6 , Table 2, entry 10, 52% ee), lit.⁶ $[\alpha]^{20}_{\text{D}}$ = +59.5 (c 0.88, C_6H_6 , >98% ee, (R)).

(S)- and (R)-(2-naphthyl)phenylmethanol (3i). The (S)-enantiomer was obtained as a solid in 92% isolated yield (Table 2, entry 7) and the (R)-enantiomer was obtained as a solid in 92% isolated yield (Table 2, entry 11); mp 70.9-71.2 °C; ^1H NMR (CDCl_3) δ = 7.75-7.85 (m, 4H), 7.20-7.47 (m, 8H), 5.95 (s, 1H), 2.36 (bs, 1H); ^{13}C NMR (CDCl_3) δ = 143.59, 141.09, 133.22, 132.85, 128.51 (2), 128.29, 128.04, 127.64 (2), 126.68 (2), 126.15, 125.94, 125.00, 124.74, 76.32; HRMS calcd for $\text{C}_{17}\text{H}_{14}\text{O}$: m/z 234.1045, found: 234.1051; The ee was determined on a Chiralcel OD-H column with heptane : isopropanol = 90 : 10, flow = 0.5 mL/ min. Retention times: 24.3 [S-enantiomer] and 28.0 [R-enantiomer] min; $[\alpha]^{20}_{\text{D}}$ = -4.8 (c 1.37, C_6H_6 , Table 2, entry 7, 53% ee), $[\alpha]^{20}_{\text{D}}$ = +6.7 (c 1.62, C_6H_6 , Table 2, entry 11, 75% ee), lit.⁶ $[\alpha]^{20}_{\text{D}}$ = +7.4 (c 0.76, C_6H_6 , 94% ee, (R)).

Identification of borate ester 4

In a flame dried Schlenk tube flushed with nitrogen, 1.55 mg (6.0 μmol , 3 mol%) of $\text{Rh}(\text{acac})(\text{C}_2\text{H}_4)_2$ and 14.0 μmol (7 mol%) of one of the enantiomers of phosphoramidite **L1** were dissolved in 2 mL of dry dioxane. After stirring for 15 min at room temperature, 0.2 mmol of substrate **1a** and 0.4 mmol of phenylboronic acid **2a** (2 equiv) were added and the resulting mixture was stirred at reflux. After 4 h the reaction mixture was cooled to RT. The reaction mixture was passed through a silica-plug and the solvent evaporated under reduced pressure. According to ^1H -NMR, a mixture was obtained of 9% starting material **1a**, 36% product **3a**, and 55% borate ester **4** with a characteristic benzhydrylic proton at 6.21 ppm. Negative ion ESI-MS using diluted NH_3 (aq.) as a base, gave a specific isotope pattern for $\text{C}_{13}\text{H}_{11}\text{BO}_3^-\cdot\text{NH}_3$ ($\text{M}-\text{NH}_4^+$): m/z 277.1 (15%,

^{10}B , ^{35}Cl), 278.1 (100%, ^{11}B , ^{35}Cl), 279.0 (25%, ^{10}B , ^{37}Cl), 280.0 (25%, ^{11}B , ^{37}Cl). Usual work-up of the mixture with aqueous ammonia 12.5% (*vide supra*), followed by flash chromatography (SiO_2 , pentane:EtOAc = 20:1) gave the product **3** in 89% isolated yield.

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